

12

EUROPEAN PATENT APPLICATION

21 Application number: 88307186.2

51 Int. Cl.⁴: **G02F 1/17** , **B60R 1/08** ,
B60J 3/04 , **B60J 1/06**

22 Date of filing: 03.08.88

30 Priority: 21.08.87 US 87891

43 Date of publication of application:
22.02.89 Bulletin 89/08

64 Designated Contracting States:
DE FR GB

71 Applicant: **GENERAL MOTORS CORPORATION**
General Motors Building 3044 West Grand
Boulevard
Detroit Michigan 48202(US)

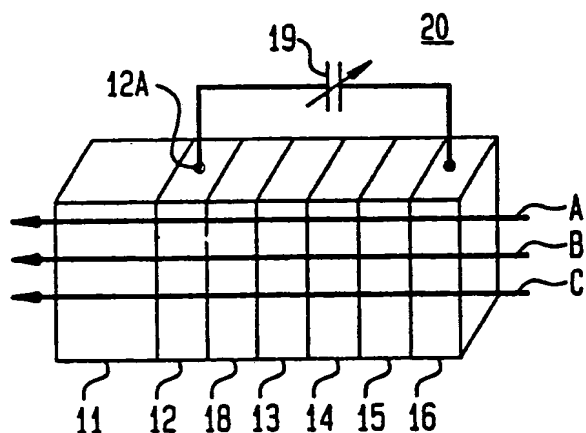
72 Inventor: **Corrigan, Dennis Arthur**
4042 Three Oaks No. 1-B
Troy Michigan 48098(US)

74 Representative: **Denton, Michael John et al**
Patent Section - Luton Office (F6) Vauxhall
Motors Limited P.O. Box 3 Kimpton Road
Luton Bedfordshire LU2 0SY(GB)

54 **Electrooptical device.**

57 An electrochromic device (20) useful as a smart window comprises a pair of transparent layers (12,16) that serve as terminal electrodes, and between which is sandwiched an electrochemical cell including a layer (13) of electrochromic material and between the layer of electrochromic material and its proximate terminal electrode layer is inserted an auxiliary layer (18) whose normal resistance is large compared to the lateral resistance of the proximate terminal electrode layer. This auxiliary layer serves to improve the lateral uniformity of the potential applied to the electrochemical cell when a voltage is applied across the terminal electrode layers with a resultant improvement in the uniformity of colouring and bleaching across the surface of the electrochromic device.

FIG. 3



EP 0 304 198 A2

ELECTROOPTICAL DEVICE

This invention relates to an electrooptical device and more particularly to such a device whose light transmittance or reflecting characteristics may be controlled by an applied electrical field. Such an electrooptical device is often termed an electrochromic device.

Electrochromic devices are of increasing importance particularly in the automotive industry and the invention will be described for specific use in such industry although a wider use clearly is apparent.

In the automotive industry, electrochromic devices would be useful in the glass portions of an automotive vehicle. More particularly, an electrochromic windshield would be useful so that the transmission of light into the passenger compartment could be regulated to facilitate the heat management of such compartment. For example, it is advantageous to control the transmittance of infrared and visible radiation from the sun into the passenger compartment during the heat of the day to reduce the load on the air conditioning requirement. Similarly, it would be desirable to reduce the transmittance of visible light through the side windows of an automobile to permit privacy to its interior when desired. As a consequence, the automotive industry is showing considerable interest in so-called "smart windows" through which light transmittance can be controlled either manually or automatically.

Additionally, there also are electrochromic applications, such as for a rear-view mirror of an automotive vehicle, in which it would be desirable to change its reflectance automatically in response to photoelectric sensing of approaching headlights, to reduce the glare on the driver of the vehicle.

Electrochromic devices typically involve a rigid passive substrate that provides structural support, such as a layer of glass, for the active portion which comprises a multilayer sandwich of elements. Generally, the two outer layers of the active portion serve as the two terminal electrodes for the electronic current of the electrochromic device. Between these terminal electrode layers are sandwiched an electrochemical cell which generally comprises in succession a layer of an electrochromic material, a layer of an electrolyte, either solid or liquid, and a counter electrode. When a dc voltage is applied across the two terminal electrode layers, electrons are either injected in or ejected out of the electrochromic layer at its interface with the terminal electrode layer while suitable ions are injected into or ejected from the electrochromic layer at its electrolyte interface. The electrolyte must conduct the ions participating in the elec-

trochemical reaction that causes the colour change. The counter electrode must be reversible to the same ions since it must allow the colour changing reaction to proceed in the reverse direction so that the electrochromic layer may be also uncoloured or "bleached" when desired. The counter electrode may also store the ions involved in the colouration reaction. In some instances, the counter electrode may also serve as one of the two terminal electrodes. For most applications, the electrolyte, the counter electrode and the two terminal electrodes need to be transparent.

The depth of colour change and the resulting transmittance change in the electrochromic layer depend on the amount of ionic charge injected into or ejected from the electrochromic layer. In one sense, an electrochromic cell is basically a battery with a visible state of charge.

A wide variety of materials are known to be useful for colouring in the manner described and include some which can be coloured cathodically in an electrochemical cell, such as tungstic oxide (WO_3) and molybdenum oxide (MoO_3), and others which can be coloured anodically in an electrochemical cell, such as iridium oxide.

Similarly, a wide range of materials have been proposed, both liquid and solid, for use as the electrolyte. Superionic conductors and polymeric ion conductors are available in solid form.

Typically, the terminal electrode layers are of transparent tin oxide doped to be highly conductive.

When an electrochromic device of the kind described has been used as the window of an automobile, the window is often subject to non-uniform colouration (darkening) and bleaching (lightening) as its transmission is varied. Such non-uniformity is undesirable and the present invention provides a solution to this problem.

An electrochromic device in accordance with the present invention is characterised by the features specified in the characterising portion of Claim 1.

It has been found that the nonuniformity in many prior art cases results from the nonuniformity in the effective potential acting on the electrochemical cell. In particular, the effective potential has a lateral variation because of the voltage drop resulting from the lateral resistance of the terminal electrode layers. The present invention is based on making more uniform the potential acting on the electrochemical cell.

To this end, in accordance with the present invention, there is included in the electronic part of the circuit between the two terminal electrode lay-

ers an auxiliary (electrically conducting) layer of a material such that the resistance normal to the surface of this auxiliary layer effectively dominates the lateral variation in the resistance of the terminal electrode layers. This normal resistance may either result from the resistance of the material in the bulk of the auxiliary layer or may result from the contact resistance introduced by the barrier between the auxiliary layer and the contiguous terminal electrode layer. As a result of the inclusion of this auxiliary layer, the potential over the entire surface of the electrochemical cell is made more uniform because the degree of lateral variation of the voltage drop in the terminal electrode layer is reduced. The resistivity of this auxiliary layer however should not be so high that excessively high voltages need to be applied to the terminal electrode layers to achieve the electrochromic effect.

The invention will now be described, by way of example, with reference to the following description taken in conjunction with the accompanying drawings, in which:-

Figure 1 illustrates schematically a cross-section of an electrochromic device typical of the prior art;

Figure 2 shows schematically a diagram of the equivalent resistance circuit of the electrochromic device of Figure 1;

Figure 3 illustrates in the manner of Figure 1 an electrochromic device in accordance with an embodiment of the invention; and

Figure 4 similarly shows schematically the equivalent resistance circuit of the embodiment of Figure 4.

A prior art electrochromic device 10 shown in Figure 1 includes the planar glass substrate 11 which provides structural support and ruggedness to the electrochromic device, but is otherwise passive. Supported on this glass substrate 11 is a stack of coatings or layers 12 through 16, of which layers 12 and 16 are the terminal electrode layers. Across these terminal electrode layers 12, 16, there is established a voltage supplied by a dc (direct current) source 19 which may be varied, either manually or electronically. Generally, these terminal electrode layers 12, 16 are of tin oxide (SnO_2) doped to increase its electrical conductivity. Such terminal electrode layers 12, 16 can be highly light-transmissive. A typical thickness for each of these terminal electrode layers 12, 16 is about 100 nanometers.

The intermediate layers 13, 14 and 15 basically form a spectroelectrochemical cell or thin-film battery whose colour is dependent on its state of charge; to colour or to bleach the spectroelectrochemical cell requires only the charge or discharge of its electrochromic film. In this spectroelectrochemical cell, intermediate layer 13 is of

the electrochromic material, intermediate layer 14 is of an ionic conductor, and intermediate layer 15 is the counter electrode, that may also be electrochromic. For example, intermediate layer 13 may be of hydrous nickel oxide $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and of a thickness of about 50 nanometers. The intermediate layer 15 that serves as the counter electrode typically may be a layer of a material such as manganese hydroxide which is both an ionic and an electronic conductor, of thickness comparable to that of intermediate layer 13. The (electrolytic) intermediate layer 14 may be of 1M potassium hydroxide, typically 100 micrometers thick.

The colouration reaction in a gross sense is similar to the anodic charging reaction in nickel oxide battery electrodes where divalent nickel oxide is oxidized to form a more coloured trivalent nickel oxide. Bleaching occurs when the reaction is reversed. The change in colouration tends to be continuous with change in the potential of the cell.

Figure 2 is an equivalent circuit schematic which illustrates the resistance experienced in the terminal electrode layer 12 to reach its electric contact 12A by the electron current (as distinguished from the ionic current in the cell portion) that is associated with the paths of three different light rays, A, B and C shown in Figure 1. Each path is through regions of the terminal electrode layer 12 successively further displaced by a unit length from the edge of the terminal electrode layer 12 where the voltage is being applied. The resistance R in Figure 2 is the resistance per unit length in the lateral direction parallel to the plane of the terminal electrode layer. A similar situation exists at the other terminal electrode layer 16. It is evident that at node 21, corresponding to the point of entry of ray A into terminal electrode layer 12, the voltage drop from the electric contact 12A, will be less than at nodes 22 and 23, corresponding to the points of entry of rays B and C into terminal electrode layer 12. This means that the voltage at node 21 will be higher than at nodes 22 and 23 so that the electrochemical cell formed by intermediate layers 13, 14 and 15 will experience a higher applied potential at the point corresponding to node 21 than it will at points corresponding to nodes 22 and 23, resulting in a different amount of colourization at the point corresponding to node 21. Similar considerations result in a different degree of colouring at the point corresponding to node 22 than at the point corresponding to the node 23. If a low resistance metal layer is deposited over all the edges of the terminal electrode layer 12 for use as the connection to a lead from the voltage supply, electric contact 12A essentially corresponds to the edge nearest the point being considered.

One solution to this problem would be to increase the lateral conductivity of the terminal elec-

trode layer 12, as could be done by increasing the thickness of the layer, since its conductivity will increase with thickness. However a trade-off with the transparency of this layer eventually needs to be made. With materials presently available for use as the terminal electrode layer 12, a limit in thickness for adequate transparency is reached before this non-uniformity problem is solved for electrochromic windows of size needed for automobile use.

Referring now to Figure 3, there is shown an electrochromic device 20 in accordance with the present invention. Electrochromic device 20 lessens the dependence of the effective potential on a particular point of the (electrochromic) intermediate layer 13 on its distance from the electric contact 12A of the terminal electrode layer 12 where the full voltage is being applied, through the use of an (added transparent) auxiliary layer 18 between the terminal electrode layer 12 and the (electrochromic) intermediate layer 13. The reference numerals used in Figure 1 are carried over to Figure 3 for corresponding elements.

This auxiliary layer 18 is chosen to have a resistance in the direction normal to the plane of the auxiliary layer which is high relative to its resistance in the plane of the auxiliary layer. The equivalent schematic circuit for electrons along paths in the terminal electrode layer 12 and auxiliary layer 18 corresponding to light rays A, B and C is depicted in Figure 4 in the manner described in connection with Figure 2. In this case, the resistance normal to the surface per unit area through this auxiliary layer 18 is R' . If the value R' is sufficiently higher than R , it is evident from the equivalent circuit depicted, that the percentage variation in total series resistance from either of the nodes 31, 32 and 33 to electric contact 12A will be less than the percentage variation in series resistance from either of nodes 21, 22 and 23 to electric contact 12A. In particular, if R' is much larger, for example by a factor of ten, than R , the resistance in each of the three paths depicted in Figure 4 will remain approximately equal to R' whereas for the three paths depicted in Figure 2, the resistances will be R , $2R$ and $3R$, respectively.

It can be appreciated that the R' resistance will be the sum both of the bulk normal resistance of the auxiliary layer 18 and of the contact resistance between the auxiliary layer and the contiguous terminal electrode layer 12. In particular, it appears that relatively high conductivity nickel oxide can be used as the auxiliary layer 18 because of the relatively high contact resistance it forms with a terminal electrode layer 12 of fluorine-doped tin oxide.

The inclusion of the (transparent) auxiliary layer 18 will necessitate a higher applied voltage to compensate for the voltage drop added by such

inclusion. However, this is not a serious disadvantage because the power dissipation by the electrochromic voltages will remain low. However, to avoid the need for an unnecessarily high applied voltage, R' advantageously is larger than R by a factor of ten to twenty.

As was previously mentioned, the problem of lateral voltage drop in a terminal electrode exists at each of the two terminal electrode layers. It is sufficient to include only one auxiliary layer to solve the problem at both terminal electrode layers if its normal resistance is sufficiently high. Typically if the two terminal electrode layers are of the same kind, a single auxiliary layer with a normal resistance per unit area of about twenty times the lateral resistance per unit length of each terminal electrode layer should be sufficient for high uniformity with convenient voltage levels.

It should be apparent that the auxiliary layer may be added anywhere in the path of the electron current as distinguished from the path of ionic current. Accordingly, the auxiliary layer may alternatively have been inserted between the (counter electrode) intermediate layer 15 and the terminal electrode layer 18 although this normally would be an inferior location. In some instances it may be preferable to add separate auxiliary layers at opposite ends, e.g. one between terminal electrode layer 12 and intermediate layer 13 and one between intermediate layer 15 and terminal electrode layer 18 to distribute the desired normal resistance between them.

At the present date, the best transparent conductor available for use as a terminal electrode layer is fluorine-doped tin oxide (FTO). If the terminal electrode layer 12 consists of an FTO coating with a resistance of 10 ohms per square, an added layer of a thickness to add a normal resistance of 100 ohms to a one square centimetre area might comprise a thickness of 10 micrometres of a material having a resistivity of 1×10^5 ohm-centimetre.

The design of a two layer coating will depend on the area of the coating. The lateral or parallel resistance of the terminal electrode layer 12 will remain constant as the area is increased provided the geometry remains the same, i.e., the two lateral dimensions are being increased by the same factor. However the normal resistance of the auxiliary layer 18 will decrease proportionally with area. Thus, the product of the auxiliary layer resistivity and its thickness must increase proportionally with area to maintain the desired ratio of parallel to normal resistance. For example, a 5000 centimetre square area, the typical size of an automobile window, requires a resistivity film thickness product 5000 times that in the one centimetre square example discussed above. As is known, the resistivity

of tin oxide can be controlled by its doping. A film of suitable resistivity is achievable by tin oxide with little or no doping.

Accordingly, in a presently preferred embodiment of the invention, each of terminal electrode layer 12 and auxiliary layer 18 will be of tin oxide with the former doped with fluorine to be highly conductive while the latter would be essentially undoped to be several orders of magnitude less conductive. Each of these layers can be readily prepared by metallo-organic deposition.

In instances where higher normal resistivities than realizable with undoped tin oxide are needed, tantalum oxide or titanium oxide may be used instead.

It should be recognized that the invention is broadly applicable to electrochromic devices of the general kind discussed in which the lateral resistance of the terminal electrode layers result in a lateral voltage drop that results in nonuniformity of the effective potential on the electrochemical cell portion of the electrochromic device with resulting non-uniform colouring and bleaching. Accordingly, the invention is not limited to the specific set of materials used in the illustrative embodiment described.

It should be appreciated that various arrangements can be used to control the transmittance of the electrochromic device. For example, provision can be made to adjust the voltage supplied by the source manually, as when a desired level of privacy is desired within the interior of an automobile provided with electrochromic windows. Alternatively, sensors can be used to adjust the voltage supplied automatically in response to environmental conditions, such as the amount of sunlight incident on an electrochromic windshield. Additionally, for use as a reflecting near-view mirror, a reflective coating would be deposited over one of the terminal electrode layers.

Claims

1. An electrochromic device (20) which includes a transparent substrate (11); a pair of terminal electrode layers (12,16) on the substrate; and means (13,14,15) forming an electrochemical cell included between the terminal electrode layers (12,16), including at least one layer (13) of an electrochromic material, characterized by an auxiliary layer (18) of highly resistive material is positioned between the electrochemical cell (13-15) and at least one of said terminal electrode layers (12,16), the auxiliary layer (18) having an electrical resistance normal to its thickness which is at least about ten times greater than the electrical resistance of its contiguous terminal electrode layer (12)

parallel to its thickness, for substantially reducing the lateral variations in potential applied to the electrochemical cell and an attendant lateral colour variation in the electrochromic device (20) when a voltage is applied across the two terminal electrode layers (12,16).

2. An electrochromic device as claimed in claim 1, in which the auxiliary layer (18) is of a material which forms a contact resistance with its contiguous terminal electrode layer (12) which is large compared to the lateral resistance of the terminal electrode layers.

3. An electrochromic device as claimed in claim 1 or claim 2, comprising a pair of auxiliary layers (18), wherein each auxiliary layer is disposed between the electrochemical cell and a different one of the two terminal electrode layers (12,16).

4. An electrochromic device as claimed in any one of claims 1 to 3, in which the layer (13) of electrochromic material is of nickel hydroxide.

5. An electrochromic device as claimed in any one of claims 1 to 3, in which the electrochemical cell comprises a layer (13) of nickel hydroxide, a layer (14) of potassium hydroxide, and a layer (15) of manganese hydroxide.

6. An electrochromic device as claimed in any one of claims 1 to 5, in which at least one of the pair of terminal electrode layers (12,16) is of tin oxide of relatively high conductivity and the auxiliary layer or layers (18) is of tin oxide of lower conductivity.

7. An electrochromic device as claimed in any one of claims 1 to 5, in which the auxiliary layer or layers (18) is of nickel oxide and its contiguous terminal electrode layer (12,16) is of fluorine-doped tin oxide.

8. An electrochromic device as claimed in any one of claims 1 to 7, in which the transparent substrate (11) is a window of at least about 5000 square centimetres in area.

9. An electrochromic device as claimed in any one of claims 1 to 7, in which the transparent substrate (11) is an automobile window.

10. An electrochromic device as claimed in any one of claims 1 to 7, in which the transparent substrate (11) is an automobile rear view mirror.

FIG. 1

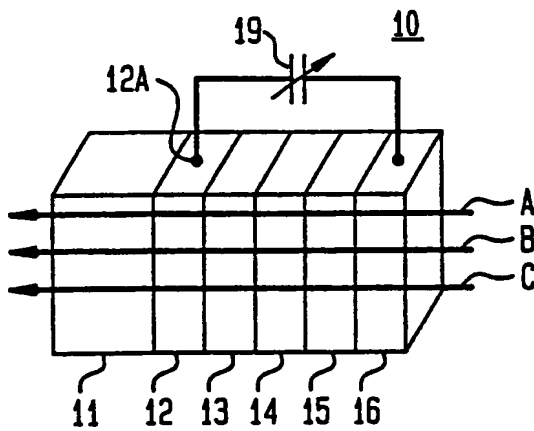


FIG. 2

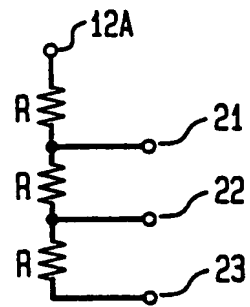


FIG. 3

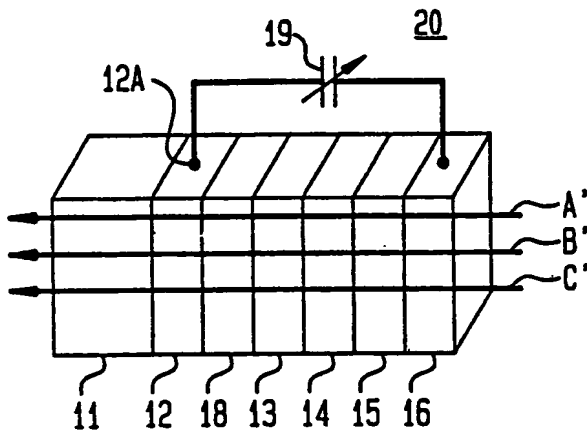


FIG. 4

